Heterogeneity of ice nucleating particles measured in Swiss alpine snow samples: supplemental information

Killian P. Brennan[1], Robert O. David[1], Nadine Borduas-Dedekind[1,2]

[1]Institute for Atmospheric and Climate Science, ETH Zurich, Zurich, 8092, Switzerland
[2]Institute for Biogeochemistry and Pollutant Dynamics, ETH Zurich, Zurich, 8092, Switzerland

Correspondence to: Nadine Borduas-Dedekind (nadine.borduas@usys.ethz.ch)

Collection procedure:

1. Collection procedure:
2. A sampling site was chosen to have as little human disturbances as possible (e.g. footprints, ski tracks etc.).
3. The person sampling wore powder free nitrile gloves (PZN-3778303, Sempermed, USA).
4. The snow was scooped directly with the open tube, to avoid contaminating the sample with hands or spatulas. If the snow was fresh, loose powder, it was necessary to compress the snow within the tube and sample multiple times to obtain a large enough sampling volume (optimal 30 mL). This compression was accomplished by repeatedly scooping snow and banging the bottom of the tube against a firm surface (for example ski boot).
5. The cap was tightly screwed back on to the tube.
6. The sampling site was documented through photography, to record the surrounding snow conditions. The identification number on the tube was also photographed to relate the sample to its sampling location and sampling time.
7. The coordinates of the site were determined via GPS and recorded.
8. The samples were placed in a freezer as soon as possible. If no freezer was readily available (for a longer, multi-day trips) the samples were stored outside in sub-freezing conditions. During transportation, insulating clothing (for example a down garment) was wrapped around the samples to prevent melting.
9. For long-term storage, the samples were placed in a freezer at -20 °C and analyzed within 14 days.

Recorded parameters

Table S1 Overview of all snow sample data. Missing ID's correspond to prepared but unused sampling tubes, the date represents the day of sampling, latitude and longitude with an accuracy of 100m, elevation of sampling site, site name extracted from map, snow age for surface samples, sampling depths for depth profiles, total organic carbon (TOC), conductivity and T_{50}.

ID	Date	lat [°N]	lon [°E]	Elevation [m a.s.l.]	Site Name	Snow age [d]	Depth [m]	TOC [mg/L]	Conductivity [µS/cm]	T50
1	04.02.18	46.679	7.400	1715	Schibe	1	0	0.39	7	-6.5
2	04.02.18	46.674	7.394	2033	Schibe	1	0	0.39	7	-5.8
3	13.02.18	46.533	7.473	2053	Rauflihore	1	0	0.35	5	-10.4
4	13.02.18	46.532	7.483	2316	Rauflihore	1	0	0.30	5	-12.3
6	24.02.18	47.044	9.112	2294	Schilt	3	0	0.30	2	-9.6
7	24.02.18	47.046	9.115	2242	Schilt	3	0	0.40	6	-19.0
8	24.02.18	47.046	9.115	2242	Schilt	3	0	0.33	4	-15.3
9	24.02.18	47.046	9.115	2242	Schilt	3	0	0.31	4	-14.8
10	01.03.18	47.415	8.541	440	Wahlenpark	0	0	2.14	10	-15.8
16	02.03.18	47.416	8.541	440	Wahlenpark	0	0	1.94	8	-16.7
17	04.03.18	46.591	7.482	1945	Meniggrat	1	0		3	-8.2
21	17.03.18	46.554	7.457	1625	Alpetli	0	0	0.67	4	-21.6
22	17.03.18	46.554	7.457	1625	Alpetli		0.2	0.62	3	-7.2
23	17.03.18	46.554	7.457	1625	Alpetli		0.4	0.60	4	-14.4
24	17.03.18	46.554	7.457	1625	Alpetli		0.6	0.57	3	-20.3
25	17.03.18	46.554	7.457	1625	Alpetli		0.8	1.33	2	-6.7
26	17.03.18	46.554	7.457	1625	Alpetli		1	0.58	3	-5.3
27	17.03.18	46.554	7.457	1625	Alpetli		1.2	0.65	3	-6.5
28	17.03.18	46.554	7.457	1625	Alpetli		1.4	0.64	3	-5.9
31	14.04.18	46.439	7.566	1954	Engstligenalp	9	0	0.81	6	-6.9
32	14.04.18	46.434	7.556	1967	Engstligenalp	9	0	0.70	3	-5.7
33	14.04.18	46.429	7.545	2185	Grossstrubel	9	0	0.58	3	-12.1
34	14.04.18	46.426	7.543	2385	Grossstrubel	9	0	0.60	4	-5.8
35	14.04.18	46.421	7.549	2638	Grossstrubel	9	0	5.17	3	-9.5
36	14.04.18	46.418	7.551	2874	Grossstrubel	9	0	0.86	4	-13.4
37	14.04.18	46.414	7.554	3091	Grossstrubel	9	0	0.60	3	-11.7
38	14.04.18	46.414	7.557	3153	Grossstrubel	9	0	0.76	4	-7.4
39	14.04.18	46.413	7.562	3222	Grossstrubel	9	0	0.97	7	-9.3
41	14.04.18	46.435	7.562	1983	Engstligenalp		1.4	0.54	2	-17.3
42	14.04.18	46.435	7.562	1983	Engstligenalp		1.3	0.59	6	-14.0

ID	Date	lat [°N]	lon [°E]	Elevation [m a.s.l.]	Site Name	Snow age [d]	Depth [m]	TOC [mg/L]	Conductivity [µS/cm]	T50
43	14.04.18	46.435	7.562	1983	Engstligenalp		1.2	0.69	3	-16.8
44	14.04.18	46.435	7.562	1983	Engstligenalp		1.1	0.42	2	-17.1
45	14.04.18	46.435	7.562	1983	Engstligenalp		1	0.56	3	-14.2
46	14.04.18	46.435	7.562	1983	Engstligenalp		0.9	0.61	6	-9.0
47	14.04.18	46.435	7.562	1983	Engstligenalp		0.8	0.63	7	-15.0
48	14.04.18	46.435	7.562	1983	Engstligenalp		0.7	0.84	9	-13.8
49	14.04.18	46.435	7.562	1983	Engstligenalp		0.6	0.41	2	-17.9
51	14.04.18	46.435	7.562	1983	Engstligenalp		0.5	0.49	2	-16.4
52	14.04.18	46.435	7.562	1983	Engstligenalp		0.4	0.34	2	-18.3
53	14.04.18	46.435	7.562	1983	Engstligenalp		0.3	0.57	3	-14.2
54	14.04.18	46.435	7.562	1983	Engstligenalp		0.2	0.47	3	-14.9
55	14.04.18	46.435	7.562	1983	Engstligenalp		0.1	0.45	3	-14.5
56	14.04.18	46.435	7.562	1983	Engstligenalp	9	0	0.63	3	-7.7
57	14.04.18	46.435	7.562	1983	Engstligenalp	9	0	0.67	4	-9.1
58	14.04.18	46.435	7.562	1983	Engstligenalp	9	0	0.57	3	-6.7
59	14.04.18	46.435	7.562	1983	Engstligenalp	9	0	0.53	3	-10.7
61	02.04.18	46.542	7.467	2045	Chalberhöri	1	0	0.72	3	-9.3
62	02.04.18	46.542	7.467	2045	Chalberhöri		0.3	0.59	2	-21.6
63	02.04.18	46.542	7.467	2045	Chalberhöri		0.7	0.49	2	-17.1
64	02.04.18	46.542	7.467	2045	Chalberhöri		1	0.47	4	-16.8
65	02.04.18	46.542	7.467	2045	Chalberhöri		1.2	0.45	2	-13.0
66	02.04.18	46.542	7.467	2045	Chalberhöri		1.5	0.76	3	-7.0
67	02.04.18	46.542	7.467	2045	Chalberhöri		1.8	0.46	2	-10.3
68	02.04.18	46.542	7.467	2045	Chalberhöri		2.1	0.41	3	-11.0
69	02.04.18	46.542	7.467	2045	Chalberhöri		2.4	0.65	3	-13.5
71	15.04.18	46.835	9.795	2822	Weissfluh	3	0	0.83	4	-6.8
72	15.04.18	46.835	9.795	2822	Weissfluh	3	0	0.86	3	-13.9
73	15.04.18	46.835	9.795	2822	Weissfluh	3	0	1.15	10	-7.1
74	15.04.18	46.835	9.795	2822	Weissfluh	3	0	0.45	2	-14.4
75	15.04.18	46.835	9.795	2822	Weissfluh	3	0	1.30	3	-10.5
76	15.04.18	46.835	9.795	2822	Weissfluh	3	0	0.67	2	-16.7
77	15.04.18	46.835	9.795	2822	Weissfluh	3	0	0.84	3	-16.0
78	15.04.18	46.835	9.795	2822	Weissfluh	3	0	0.96	3	-16.4
79	15.04.18	46.835	9.795	2822	Weissfluh	3	0	1.03	3	-16.1

ID	Date	lat [°N]	lon [°E]	Elevation [m a.s.l.]	Site Name	Snow age [d]	Depth [m]	TOC [mg/L]	Conductivity [µS/cm]	T50
83	22.04.18	46.169	7.992	3530	Fletschhorn	10	0	0.82		-12.9
84	22.04.18	46.166	7.987	3227	Fletschhorn	10	0	0.94	5	-12.3
88	22.04.18	46.168	8.003	3981	Fletschhorn	10	0	0.64	14	-16.2
93	12.05.18	45.945	6.967	3137	Pte Aig. Verte	1	0	3.32		-9.5
96	12.05.18	45.944	6.962	3388	Pte Aig. Verte	1	0	1.22	13	-13.1
97	12.05.18	45.945	6.967	3137	Pte Aig. Verte	1	0	3.31	8	-10.5
98	25.04.18	46.980	8.257	2020	Pilatus	9	0	1.02	6	-7.8
99	25.04.18	46.980	8.257	2020	Pilatus	9	0	0.77	4	-6.2
101	21.05.18	47.007	9.014	2772	Vrenelisgärtli	2	0	1.87	6	-11.4
102	19.04.18	47.252	9.341	2416	Säntis	4	0	0.47	2	-15.3
103	19.04.18	47.252	9.342	2416	Säntis	4	0	0.55	2	-11.4
104	12.05.18	45.944	6.962	3388	Pte Aig. Verte	1	0	3.16		-12.3
105	19.04.18	47.252	9.342	2416	Säntis	4	0	0.60	2	-12.7
106	21.05.18	47.007	9.014	2772	Vrenelisgärtli	2	0		8	-11.6
107	21.05.18	47.007	9.014	2772	Vrenelisgärtli	2	0	1.33	7	-12.6
108	19.04.18	47.252	9.342	2416	Säntis	4	0	0.60	3	-15.1
109	21.05.18	47.007	9.014	2772	Vrenelisgärtli	2	0	1.19	6	-11.8
111	22.04.18	46.598	8.604	2729	Sankt Annafirn	11	0	0.92	2	-13.5
112	22.04.18	46.598	8.604	2729	Sankt Annafirn	11	0	0.87	2	-13.8
113	22.04.18	46.598	8.604	2729	Sankt Annafirn	11	0	0.84	2	-12.5
114	22.04.18	46.598	8.604	2729	Sankt Annafirn	11	0	1.49	2	-12.8
116	22.04.18	46.598	8.604	2729	Sankt Annafirn	11	0	0.89	2	-14.5
119	22.04.18	46.598	8.604	2729	Sankt Annafirn	11	0	1.03	2	-13.6

Techno Plastic Products tube washing comparison

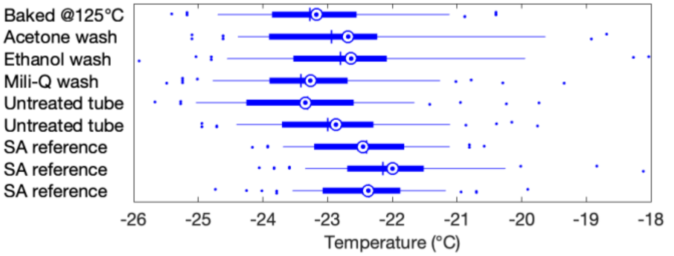

Figure S1: Comparison of different washing procedures of the Techno Plastic Products tubes as well as Sigma Aldrich references and untreated tubes.

Immersion freezing experiments with DRINCZ

The DRoplet Ice Nuclei Counter Zurich (DRINCZ) technique used in this study is described in-depth by (David et al., 2019). Briefly, a Microsoft Lifecam HD-3000 camera takes snapshots (every 15s) of a 96-well non-skirted multi-well tray (VWR, 732-2386) partially submerged in a thermostat-controlled ethanol cooling bath (Lauda Proline RP 845). To ensure that contaminants do not enter the wells of the well plate during the experiment, the plate is covered with a transparent plastic foil (PCR-TS, Axygen by Corning, USA). Mounted above the well plate, the camera monitors the light transmission through the wells supplied by an LED lighting device located at the bottom of the ethanol bath. To obtain the number of frozen wells as a function of temperature, the thermostat cools the ethanol at a rate of 1 ˚C min^{-1} until every well is frozen. This cooling rate allows for the freezing to be reported approximately every 0.25 ˚C in the range of – 25 °C to 0 °C. The number of frozen wells that freeze between pictures can be assigned to the corresponding well temperature, thus, providing the frozen fraction spectrum of the sample. NX-illite as a standard INP material has also been measured on DRINCZ with good agreement against other drop freezing assay setups (Hiranuma et al., 2015).

For analysis with DRINCZ, the snow sample in the polypropylene tube was gently melted in a stirred water bath at room temperature. Then, 5.5 mL of the liquid sample were poured into a 50 mL polystyrene reagent reservoir (89094-680, VWR, USA). Using an 8-channel electronic pipette (1613-0412, VWR, USA), each well of the well plate was filled with 50 ± 2 µL of the sample.

Frozen fraction and INP concentration analysis

DRINCZ yields images of the well plate as a function of temperature. The frozen fraction (FF) value is extracted from the images by analysing the change in light intensity of each well. The temperature step with the greatest change in light intensity of a well is assumed to coincide with the sample in that well freezing, and this temperature is referred to as T_{frz}. The FF is the ratio between the number of wells frozen at a given temperature ($n_{frz}(T)$) and the total number of wells ($n_{tot} = 96$). An FF curve as a function of temperature is then derived according to Eq. 1. The frozen fraction rises with decreasing temperatures.

$$FF(T) = \frac{n_{frz}(T)}{n_{tot}} \quad (1)$$

In order to extrapolate the *FF* determined by DRINCZ into an INP concentration relevant for atmospheric modelling, Poisson distribution calculations were used (Vali, 1971, 2019). The probability of INPs occurring in a well within the well plate can be expressed as a function of number of INPs per volume of sample in a well (Figure 2 in the main text). For freezing to occur at temperatures above the SA background, the well must contain at least one INP for freezing to occur, and multiple INPs in one well can be represented by a Poisson distribution. These statistics further assume that each INP has identical freezing efficiencies. The total INP concentration c[INP] is evaluated by summing the INPs of all the wells together and normalizing by the number of wells and the sampled volume (Eq. 2).

$$c[INP] = \frac{\sum INP}{(96\, wells)(50 \times 10^{-3}\, mLwell^{-1})} \quad (2)$$

The INP concentration ($c[INP]$) can be calculated from *FF* through Poisson distribution(Vali, 1971, 2019):

$$c[INP] = -\frac{1}{V_d} \ln(1 - dFF) \quad (3)$$

where V_d is the droplet volume and dFF is the change in FF. For example, a FF of 0.5 corresponds to an INP concentration of 14 INPs mL^{-1}.

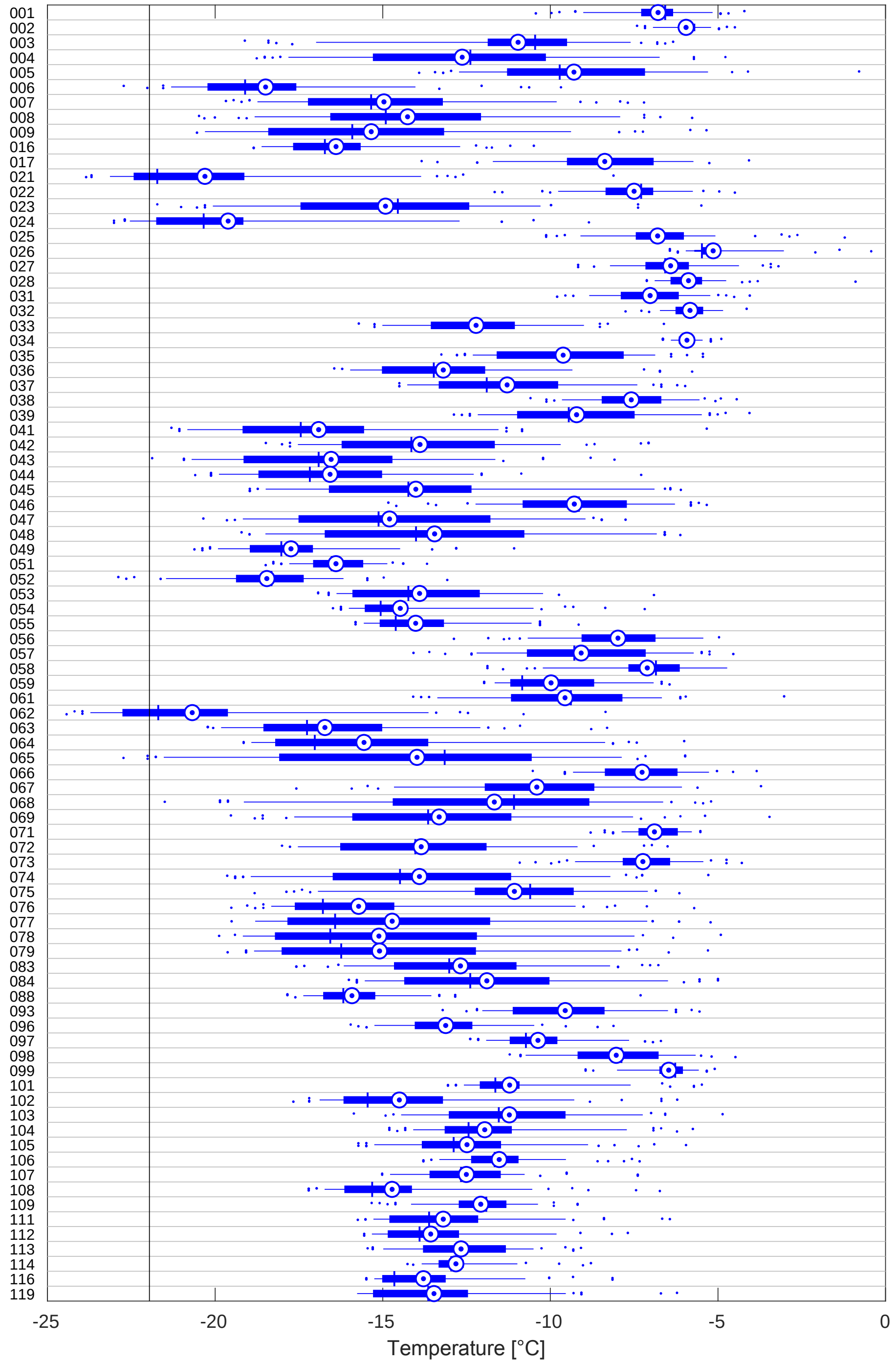

Figure S2 Summary of recorded freezing profiles of each sample. Boxes show 25-75th quantile, whiskers show 5-95th quantile, the concentric dot and ring show the mean (*T_{50}*) and the thin vertical blue line represents the median. Outliers are displayed as dots and are randomly scattered vertically to avoid overlapping. The grey shaded area shows the 25-75th quantile range of the Sigma Aldrich water background, with its mean as the solid black line.

Size dependency

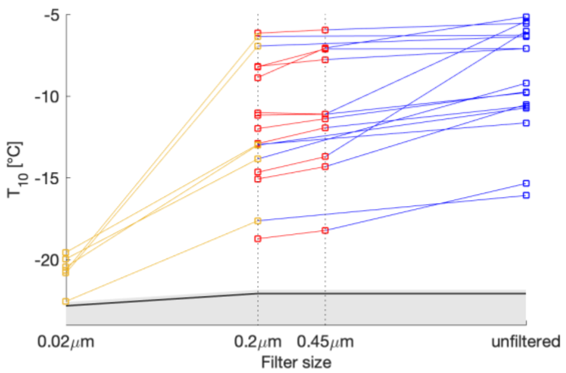

Figure S3: T_{10} as a function of filter size for select samples. Sigma Aldrich water background T_{10} is shown in black and the respective standard deviation is shaded in grey. The samples were filtered at 450, 200 and 20 nm and the lines connect the different filtrates of the same sample. The T_{10} version of this graph can be found in the supplementary information.

Engstligenalp

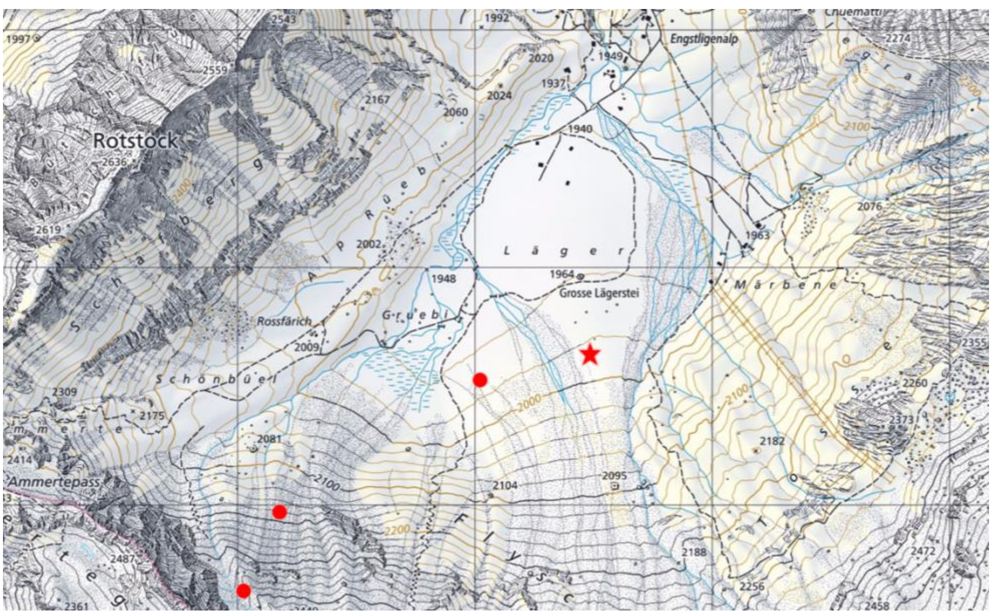

Figure S4: Topography overview of the Engstligenalp site. The star shows the sampling site of the sample marked as origin and distances 10, 20 and 30 m in Figure 7. The circles show the locations of the other tree sampling sites. Reproduced with permission of © swisstopo, 2019 (BA19060).

Site images

Figure S5: Selected site images with respective ID number.

References

David, R. O., Cascajo, M. C., Brennan, K. P., Rösch, M., Els, N., Werz, J., Weichlinger, V., Boynton, L. S., Bogler, S., Borduas-Dedekind, N., Marcolli, C. and Kanji, Z. A.: Development of the DRoplet Ice Nuclei Counter Zürich (DRINCZ): Validation and application to field collected snow samples, Atmospheric Meas. Tech. Discuss., submitted, 2019.

Hiranuma, N., Augustin-Bauditz, S., Bingemer, H., Budke, C., Curtius, J., Danielczok, A., Diehl, K., Dreischmeier, K., Ebert, M., Frank, F., Hoffmann, N., Kandler, K., Kiselev, A., Koop, T., Leisner, T., Möhler, O., Nillius, B., Peckhaus, A., Rose, D., Weinbruch, S., Wex, H., Boose, Y., DeMott, P. J., Hader, J. D., Hill, T. C. J., Kanji, Z. A., Kulkarni, G., Levin, E. J. T., McCluskey, C. S., Murakami, M., Murray, B. J., Niedermeier, D., Petters, M. D., O'Sullivan, D., Saito, A., Schill, G. P., Tajiri, T., Tolbert, M. A., Welti, A., Whale, T. F., Wright, T. P. and Yamashita, K.: A comprehensive laboratory study on the immersion freezing behavior of illite NX particles: a comparison of 17 ice nucleation measurement techniques, Atmospheric Chem. Phys., 15(5), 2489–2518, doi:10.5194/acp-15-2489-2015, 2015.

Vali, G.: Quantitative evaluation of experimental results an the heterogeneous freezing nucleation of supercooled liquids, J. Atmospheric Sci., 28(3), 402–409, doi:10.1175/1520-0469, 1971.

Vali, G.: Revisiting the differential freezing nucleus spectra derived from drop-freezing experiments: methods of calculation, applications, and confidence limits, Atmospheric Meas. Tech., 12(2), 1219–1231, doi:https://doi.org/10.5194/amt-12-1219-2019, 2019.